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# ABSTRACTS

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This book is a collection of abstracts of presentations given at the International Symposium on Structure and Bonding in Noncrystalline Solids, 23-26 May 1983, Reston, Virginia, USA.



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On behalf of the
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*The Chairmen*

# NORMAL STRUCTURAL BONDING AND DEFECTS IN COVALENT AMORPHOUS SEMICONDUCTORS

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Although the 8-N rule of covalent bonding is generally obeyed in amorphous semiconductors, well-defined centers exist and these control the electronic properties of the solids. The defects have two distinct reasons for their presence--they can arise from either strains upon material prepration or thermodynamic considerations. The strain-related defects characterize those amorphous solids in which the average coordination number is larger than approximately 2.4, their concentration is ordinarily very sensitive to the preparation techniques. In contrast, thermodynamically induced defects arise because of their low creation energy, and a minimum concentration characterizes any given material. These ideas have led to a resolution of several major puzzles with regard to the electronic properties of the two major classes of amorphous semiconductors--chalcogenide glasses and amorphous silicon-based alloys. Pure amorphous silicon is overconstrained and has large defect densities, but these can be reduced by many orders of magnitude if the material is alloyed with monovalent atoms such as hydrogen or fluorine. On the other hand, amorphous $As_2Se_3$ always contains a high defect density, for thermodynamic reasons. In addition to the concentration of defects present in a given material, its electronic properties depend critically also on the <u>nature</u> of these defects. In particular, the sign of the effective correlation energy of the defect with the lowest creation energy is of the utmost importance.

# A STATISTICAL MECHANICAL MODEL FOR CHEMICAL DISORDER IN INTERACTING: APPLICATION TO BORATE AND SILICATE GLASSES

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The present model provides a formalism for studying the effects of chemical disorder in a system of interacting atoms in which the number of neighbors of each kind of atom need not be the same. When they are the same, this model reduces to the quasi-chemical approximation.

The technique is applied to a model for phase separation in alkali silicates and alkaline-earth silicates in which the non-bridging oxygens are highly associated. A miscibility dome similar to that observed in sodium silicates, barium silicates, and calcium silicates is predicted. The suppresion of phase separation in the alkaline-earth silicates is predicted.

The technique is extended to systems in which the composition in terms of structural units is not fixed. This extension is used to study several simple models for the alkali-borate glasses. Applied to one of the models, the technique predicts the fraction of tetrahedrally coordinated boron atoms($N_4$) as a function of alkali content at low temperatures which is in agreement with the work of Bray and Yun* and not inconsistent with their suggestion of the extensive occurrence of the diborate group. A relationship between $N_4$ and composition at elevated temperatures is predicted.

*Bray, P. J. and Yun, Y. H. (1978), J. Non-Crystalline Solids 27 363.

# STUDIES OF SHORT-RANGE ORDER IN METALLIC GLASS ALLOYS: APPLICABILITY OF EXTENDED X-RAY ABSORPTION FINE STRUCTURE

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Metallic glasses are characterized by a lack of long-range order in their atomic structure, but have been found to possess significant order within distances corresponding to the first two or three neighbor shells. This short-range order is important in relating physical properties of glass alloys to composition and/or chemistry. Few analytical methods permit straightforward exploration of atomic scale order in noncrystalline samples. The fine structure in x-ray absorption edges is known to be due to interactions between the absorbing atom and its neighbors and in particular is sensitive to the number of neighbors and the interatomic spacings. Extended x-ray absorption fine structure spectroscopy (EXAFS) is a technique aimed at deducing details of local ordering from measurements of the absorption coefficient in an energy range just above an edge. There are some difficulties in applying this technique to noncrystalline materials and the purpose of this paper is to explore quantitatively some of the proposals for circumventing the problems. The approach is to invert the experimental procedure: rather than deducing atomic structure from measured EXAFS, the EXAFS spectrum will be calculated using well defined procedures and based on computer generated models of the glass structure. It is found that most of the EXAFS spectrum can be reproduced from models using the simple single scattering formulation of the interference phenomenon responsible for the fine structure. In fact, it is observed that the simple formulation works better in noncrystalline materials because of cancellation (due to spherical averaging) of multiple scattering effects. By comparing experimental spectra to those calculated at various levels of approximation, it is shown that it is possible in principle to deduce information about neighbor shells beyond the first. This process should be simplified significantly by the use of models and the procedures described in this paper to deduce modifications of the tabulated amplitudes and phase shifts needed in the analysis.

THEORY OF PROPERTIES OF $SiO_2$ AND $BeF_2$ GLASSES: A MOLECULAR DYNAMICS STUDY*

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A theory of the properties of liquid and glassy $SiO_2$ and $BeF_2$ is presented based on molecular dynamics simulations of $BeF_2$. The fluid or glass structures is basically a continuous random network, a 3-dimensionally interconnected network of $BeF_4$ (or $SiO_4$) tetrahedra, jointed at the vertices with fluctuating angles and random relative orientation of tetrahedra. It is always found that there are defects, which are atoms of high coordination number - 3-fold anions and 5-fold cations. The defects are thermally activated, the number decreasing reversibly with decreasing temperature. The importance of the defects is that diffusion takes place only at defect sites, so that separation of nearest neighbor Be-F pairs occurs only at the sites of 3-fold fluorine and 5-fold Be. Finally, it is observed that some defect sites are weakly bound.

These observations are the basis of a theory of the properties of liquid and glassy $SiO_2$ and $BeF_2$. Topics addressed are: The lack of a change in specific heat at the glass transition temperature; prediction that the viscosity of the melt will decrease with increasing pressure; a microscopic model of anamalous low-temperature excitations, including two-level systems; a rationalization of the densification and annealing of silica below the glass transition temperature. A number of new viscoelastic experiments are predicted.

*Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

# NMR STUDY OF STRUCTURE AND BONDING IN GLASSES*

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Nuclear magnetic resonance (NMR) techniques have been employed to study the bonding between atoms, and arrangements of atoms, in glasses. Oxygen bonding in $SiO_2$ and $B_2O_3$ has been investigated using the oxygen-17 isotope. The $O^{17}$ NMR spectrum for vitreous $SiO_2$ (v-$SiO_2$) exhibits well-defined structure and indicates significant local order in the material. Matching of experimental and computer-simulated spectra permits extraction of the $O^{17}$ quadrupole coupling parameters which are analyzed to obtain charge densities in the electronic orbitals and the Si-O-Si bond angles and distributions. Comparisons can be made with values obtained from the $O^{17}$ NMR spectrum of $\alpha$-cristobalite. Both boron and oxygen have been studied in v-$B_2O_3$. The $B^{10}$, $B^{11}$, and $O^{17}$ NMR spectra yield quadrupole parameters, bond angles, and charge densities. Two distinct types of oxygen site are clearly revealed which are consistent with the boroxol ring oxygens and the ring-connecting oxygens. $B^{10}$ studies of $Na_2O$-$B_2O_3$ and $Li_2O$-$B_2O_3$ glasses yield spectra which are beautifully simulated by adding the spectra from the crystalline compounds in the respective systems. The relative amount of the structural grouping (i.e. boroxol, diborate, metaborate) from each compound can then be determined in each glass and followed as a function of composition. $B^{11}$ studies in the technologically important sodium borosilicate system have permitted construction of structural models for the glasses in this system. The models yield the amount of each type of borate grouping present in each glass.

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# SLOW FRACTURE MODEL BASED ON STRAINED SILICA STRUCTURES

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A recent model[1] for environmentally controlled fracture of silica glass proposes specific chemical reactions with mechanically strained crack tip bonds. Infrared measurements on dehydroxylated silica powders[2] show that chemicals which are dissociatively chemisorbed at surface strained bond sites are the same chemicals which cause stress corrosion. The structure of the strained surface site is interpreted as edge sharing silicon/oxygen tetrahedra analogous to the structure of silica W[3], which possess Si-O bond angles and lengths far different than other polymorphs of silica. The observed effects of these bond distortions on chemical reactivity agree with molecular orbital calculations[4] performed on silicic acid clusters. Crack velocity data for silica in different chemical environments suggest that strained defect sites much as those discussed above must be produced at the crack tip before active chemical can be adsorbed and react to produce a stress corrosion effect. It is suggested that studies concerning the chemical reactivity of silica polymorphs containing strained Si-O bonds are useful in interpreting the micromechanics of glass fracture.

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# ANNEALING RADIATION-INDUCED DAMAGE IN MOS DEVICES

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It is likely that for a wide range of phenomena in MOS device oxides the rate limiting step is the diffusion of some species to the reaction site. Experimental evidence for this hypothesis based on isochronal and isothermal anneals will be presented and analyzed. These results will be compared with the work of Griscom (1) on the annealing of E′ centers in bulk fused silicon.

The principal facts to be emphasized are: (A) Most literature data for isochronal anneals of MOS devices fall into two broad bands. For half hour isochronal anneals, defect concentrations are reduced by a factor of 10 either at about 325 C or about 500 C. (B) The above mentioned data can be resonably fit by Waite's model for diffusion-limited reactions (2). (C) MOS transistors of varying gate geometry have been compared (3). Transistors with a short gate show a higher defect concentration after irradiation (prior to annealing), but anneal at lower temperatures. (D) Higher radiation doses appear to result in slower annealing.

We will attempt to combine the above facts into a consistent picture of annealing of defects in MOS oxides.

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COMPUTER SIMULATION OF THE STRUCTURE OF VITREOUS SILICA

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Several attempts have been made previously to simulate the structure of vitreous phases. Bell et al (1-2) pioneered in this field by building physical models for vitreous silica based on the random network theory, adhering to the Zachariasen's rules (4). Although this work gave reasonable results, the technique employed was rather tedious and involved meticulous care in building the physical models (3). Moreover, there is very little flexibility in testing different models and ideas by this technique.

The availability of the modern computers opened a new era in the structural simulation of the vitreous phases. Molecular dynamics technique involves essentially solving Newtonian equations of motion for a system containing a small number of atoms or molecules, where as Monte-Carlo simulation involves random movement of atoms within specified constraints (5).

This paper deals with a novel method for the simulation of the structure of vitreous silica. The bond angle (Si-O-Si) and bond length (Si-O) distributions are already available from X-ray scattering studies (6). Making full use of this information, a target bond angle and bond length distribution is achieved with two different starting structures, viz. cristobalite and quartz. Starting cartesian co-ordinates of about 500 atoms are transformed into internal co-ordinate system where distortions are easily carried out until the target distribution is obtained. Later, these internal co-ordinates are transformed back to the cartesian system where calculation of the physical properties like density and void space distribution can be carried out. Mathematics involved in this technique, and the results obtained (including stereoscopic illustrations) will be presented.

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# ELECTRONIC STRUCTURE CALCULATION OF AMORPHOUS $SiO_2$ AND $SiO_x$.*

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## ABSTRACT

The electronic structures of intrinsic amorphous $SiO_2$ and $SiO_x$ are studied by large scale microscopic calculations. Atomic structural models with periodic boundaries are constructed and computer-relaxed which give radial distribution function in close agreement with experiment. A first-principles orthogonalized linear combination of atomic orbital method is then applied to each model to obtain one-electron energy states and wave functions. Results are analyzed in terms of density of states (DOS) and partial DOS, effective atomic charges and the localization index for each electron state. These results are critically compared with experiments and correlated to the structural properties of the models. In case of a-$SiO_2$, no localized electron states are found near the conduction band edge but a mobility edge of about 0.2 eV is estimated for the valence band edge. For a-$SiO_x$ structures, it is concluded that the microscopic random bond model is more appropriate than the random mixture model. Extension of these type of calculations to other glassy systems such as $(Na_2O)_x(SiO_2)_{1-x}$ and $Cu_xZr_{1-x}$ will also be discussed.

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# ORIGIN OF URBACH EDGE IN SILICON AMORPHOUS HYDRIDE

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Measurements in the Urbach region of the optical absorption edge and time-of-flight measurements of the hole drift mobility in hydrogenated amorphous silicon, enable us to show that, the simplest explanation for the Urbach edge in amorphous silicon, namely that it is due to valence band tailing into the forbidden gap, is consistent with experiment. The absorption edge has been studied on a variety of glow discharge films, by optical transmission and photoconductivity. Significant differences in bandgap $E_g$ and the exponential absorption edge parameter Eo are observed with small changes in deposition conditions, and a physical explanation is proposed for the observed relation between $E_o$ and $E_g$.[1] The variability in $E_o$ and $E_g$ means that a comparison of the optical edge with the density of states requires that both quantities be measured on the same sample. To this end we have studied the optical absorption edge and the temperature dependence of the hole drift mobility by the time-of-flight technique on the same sample. Recent work has demonstrated that the density of states in the band tails can be determined from the temperature dependence of the electron and hole drift mobilities and their dispersion. In this picture (the multiple trapping model), the density of states distribution is strongly over-determined by time-resolved transport experiments; nevertheless, the data is found to be consistent with an exponential valence band tail with a characteristic width that matches the Urbach tail.[2] We conclude that the Urbach edge in amorphous silicon reflects band-tailing into the forbidden gap and is not an energy dependent matrix element effect.

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# STRUCTURAL IMPLICATIONS ABOUT COVALENT ALLOYS FROM BOND EQUILIBRIUM THEORY*

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A statistical mechanical theory for bond equilibrium, originally developed to describe behavior of bond defect atoms, can be used to gain insight into the structure of glasses formed from covalently bonded alloys. The theory permits one to evaluate for simply-connected chain polymers (containing no closed loops) the effect of the polymer statistics on the concentrations of one-fold (1F) bonded constituents, which are chain terminators, and three-fold (3F) bonded constituents, which create chain branches. The equilibrium concentration of an n-F constituent contains a factor $p_n$ whose value depends on the average number of chain branches $\lambda$ per polymer molecule. When $\lambda >> 1$, $p_1 \propto \lambda$ and $p_3 \propto \lambda^{-1}$. Since $\lambda = 2c_3/(c_1-c_3)$ where $c_n$ is the concentration of n-F constituents, equilibrium can only occur with $c_3<c_1$. BET has been extended to describe polymers containing closed loops by treating any part of a molecule containing one or more loops as a molecular constituent in a simply-connected structure. The concentration of a molecular constituent which has n external branches contains the same factor $p_n$ as an n-F atomic constituent, as well as other factors related to the structure of the cluster. Some of the latter are not easily calculated. But the theory may possibly be applied using empirical parameters, because it is expected that a dominant role is played by a relatively few types of clusters of a minimum size consistent with the steric constraints. In a network forming alloy such as $As_xSe_{1-x}$, the 1F clusters play a key role in maintaining a finite $\lambda$. It is expected that the dominant 1F cluster species will change with x so as to maintain a composition as close as possible to the average composition.

*Research supported by NSF grant DMR 80-23682.

# A PROOF OF THE NECESSITY OF A LOW TEMPERATURE EQUILIBRIUM PHASE IN POLYMER GLASSES

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This talk is concerned with polymeric non-crystalline solids. We first endeaver to show that certain polymeric systems are inherently non-crystalline. The proof is given in the context of the lattice model. It is shown that certain shapes can not pack in regular array at high density. The fundamental reason is that polymer dimensions vary as the square root of molecular weight, $M^{1/2}$, while in a space filling crystal the distance between adjacent polymer molecules must vary as $M^{1/3}$. Packing in regular array would result in extensive overlap which is of course prohibited by steric considerations. If the energetics of the molecules are such that the random coil form is preferred as in atactic polymers (volume proportional to $M^{3/2}$) then a glass results as an equilibrium phase. If the energetics are such that the low energy form has a volume proportional to M (linear dimensions proportional to $M^{1/3}$) then the crystalline form occurs. Thus, the inherent amorphous character of some polymeric systems necessitates the construction of a low temperature equilibrium theory of polymer glasses. This has been done and the predictions accord well with experiments. Variation of the glass temperature as a function of (1) molecular weight, (2) copolymer composition, (3) plasticizer content, (4) blend composition, (5) cross link density and strain tensor in a rubber, (6) pressure, and (7) the specific heat discontinuity at the glass transition have been accurately predicted. The very difficult problem of correctly relating the kinetics to the underlying equilibrium properties of glasses remains a major unsolved problem.

# THE CORRELATED BARRIER HOPPING MODEL FOR A.C. CONDUCTIVITY IN GLASSES

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The phenomenon of a nearly linear frequency dependent conductivity is universally found in amorphous non-metallic materials, as well as in certain other covalent materials having a certain degree of disorder. Whilst this behaviour at first sight appears to be universal in character, there are in fact subtle, but important, differences between different classes of materials. Notably, the a.c. conductivity behaviour of amorphous chalcogenide materials (containing O,S,Se,Te) is markedly different from that exhibited by other amorphous semiconductors.

A feature which distinguishes chalcogenide materials from others is the likelihood that structural bonding defects (dangling bonds) are spin-paired as a result of the strong electron-phonon coupling characteristic of such materials. Thus the defects can be viewed as being oppositely charged, diamagnetic entities.

We have developed a theory for a.c. conduction in chalcogenide materials which takes as its mechanism the hopping of two electrons between such defects under the influence of an applied alternating electric field. A central feature of this model is that the electrons hop over a potential barrier between two sites, whose height is correlated with the inter-site separation (so-called correlated barrier hopping). This theory is able to account for previously puzzling correlations between the magnitude of the a.c. conductivity (and the frequency exponent) with the d.c. conductivity (or equivalently the band-gap). Recent developments in this theory will be reviewed, including the possibility of non-random distributions of defect centres in glasses, and single electron hopping between a charged defect and a neutral, paramagnetic centre as an explanation of high temperature behaviour. Certain unexplained aspects of the phenomenon, such as the marked decrease in the temperature dependence of a.c. conductivity at very low temperatures, will be discussed.

FUNDAMENTAL MODELS OF ELECTRONIC TRANSPORT IN AMORPHOUS SEMICONDUCTORS†

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Electronic excitations in condensed matter either are quasi-free or self-trap. This fundamental dichotomy results in two distinct models of electronic carriers in amorphous semiconductors. In one the predominant charge carriers behave as quasifree particles; in the other they form small polarons and move by small-polaronic hopping. The salient features of the electronic transport arising from the high-mobility (Mott-CFO) model and the small-polaron model are contrasted. While some amorphous semiconductors support high-mobility transport many of the commonly studied materials (e.g. chalcogenide glasses) display small-polaron transport.

†This work performed at Sandia National Laboratories supported by the U.S. Dept. of Energy under contract DE-AC04-76-DP00789.

ELECTRONIC PROPERTIES OF $SiO_2$ AND MODELS FOR ITS POINT DEFECTS*

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The electronic band structure of silicon dioxide in several crystal structures is now well established[1] and can be understood in terms of simple tight-binding considerations[2]. Similar progress has recently been made for amorphous[3] $SiO_2$, whose electronic properties show striking similarities to those of crystalline $SiO_2$. This knowledge, in turn, can be used to consider the transport properties of electrons and holes[4] and mechanisms for defect creation[5] by ionizing radiation. It also forms a starting point for the development and analysis of defect models[6], although detailed work on these requires special theoretical techniques. In this talk I will follow this line of reasoning, concluding with a discussion of $SiO_2$ defect models, with particular reference to the question of vacancy-interstitial defects vs. valence alternation pairs.

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# RAMAN STUDIES OF REGULAR RINGS IN GLASSES*

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An energy minimization argument has been proposed[1] and refined,[2] to predict that small order rings of bonds in a glass are likely to be regular. When applied to vitreous (v-) $SiO_2$ the argument predicts substantial (~1%) concentrations of planar 3-fold and regular 4-fold rings of Si-O bonds. These hexagon-like and puckered octagon-like structures have been identified respectively with the 606 $cm^{-1}$ and 495 $cm^{-1}$ Raman lines, and are especially interesting because they do not exist in any known form of crystalline $SiO_2$. Numerous experimental results supporting the identification will be discussed, including recent isotopic substitution[3a,3b] and annealing[4] experiments. Arguments disfavoring several earlier identifications for the defect lines will also be given. The energy minimization argument will be applied to several other glasses and the predictions compared with appropriate experiments, where the latter are available. For example, the energy argument predicts that nearly planar 3-fold rings should play a large role in the structure of v-$GeO_2$, and this is consistent with our Raman studies involving isotopic substitution.[3c]

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# STRUCTURAL INVESTIVATION OF SOME AMORPHOUS INORGANIC MATERIALS : CRYSTAL CHEMISTRY, A TOOL FOR INTERPRETING LARGE ANGLE X-RAY SCATTERING STUDIES

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Structural and conformation informations about amorphous materials can be extracted and/or checked by Large Angle X-ray Scattering (LAXS).

1. Coordination Schemes : Manganese-Adenosine triphosphate and Copper-(Glycyl-L-Leucine)-Cytidine Complexes. The LAXS investigations of the amorphous form of the $Mn(II)(ATP)(H_2O)_4Na_2$ complex leads to : (i) ATP is tetracoordinated by one nitrogen atom N(7) of the puric base and one oxygen atom of each phosphate group; (ii) the octahedral environment of Mn is achieved by two water molecules. The basic structural model of the copper complex has been established. The copper atom, in a square-planar environment, is tricoordinated to the peptide residue and monocoordinated to the pyrimidine base of the nucleoside. Dihedral angles have been refined.

2. Architecture of an amorphous splat-cooled $V_2O_5$. The analysis of the experimental radial distribution shows that there are drastic changes in the vanadium coordination compared with the crystalline $V_2O_5$. The oxygen coordination around the vanadium atoms is tetrahedral. The proposed structure is based on sub-units of three $VO_4$ tetrahedra, the relative orientation of which has been determined. The $V_2O_5$ formula is retained by following the rule that each tetrahedron shares three corners with other $VO_4$ tetrahedra.

3. Unidimensional Magnetic Compounds : $MM'(EDTA)(H_2O)_4$, $2H_2O$. The magnetic studies of these compounds (MM' = CoNi or NiNi), which exhibit antiferromagnetic interactions, indicate that the amorphous materials comprise infinite chains built up with alternated "hydrated" and "chelated" octahedra bridged by carboxylate groups. Structural features : (i) hexacoordination of the EDTA ligand towards the M' atom and two bridging carboxylate groups ; (ii) a partial refinement of the MM'M chain angle and of the bridging group geometry has been achieved.

# APPLICABILITY OF THE MOLECULAR DYNAMICS TECHNIQUE TO SIMULATE THE VITREOUS SILICA SURFACE

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The pristine vitreous silica ($v-SiO_2$) surface was simulated using the molecular dynamics technique. Surface structure and composition were evaluated using concentration profiles, radial distribution functions, and bond angle distributions. Concentration profiles of constituent species as a function of depth below the surface showed the predominance of oxygen atoms rather than silicon atoms at the outer surface. The Si-O-Si bond angle distribution for bonds within several angstroms of the surface showed an additional peak near 110°, which is indicative of the presence of strained siloxane bonds at the surface. Non-bridging oxygen (NBO) as well as bridging oxygen were formed at the surface. The Si-NBO interatomic spacing was approximately 0.08Å less than the normal Si-bridging oxygen spacing and is in accordance with calculations made from spectroscopic data of defects in $v-SiO_2$. Calculations of the possible concentration of silanols (had water been present) gave results similar to those formed experimentally.

These results are significant in that they indicate the applicability of using the molecular dynamics technique to accurately simulate the $v-SiO_2$ surface.

# VIBRATIONAL STUDIES OF GLASS STRUCTURE AND LOCALIZED INTERACTIONS

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Infrared absorption and Raman spectroscopic measurements of binary alkali oxide containing silicate, phosphate, and borate glasses yield features assignable to predominantly ionic cation site interactions in addition to network vibrations characteristic of the glass former oxide. Intense bands observed in Far IR spectra are assigned to vibrations of cations at localized sites in the glass. These features exhibit marked frequency shifts with cation mass, cation charge and glass stoichiometry but show little dependence on the nature of the glass former oxide. Bulk glass properties, including glass transition temperature and conductivity activation energy, scale with cation-site frequency which is an important parameter in models describing such phenomena.

In contrast to the localized mode observed in Far IR spectra of binary oxide glasses, Raman spectra of these materials reveal features arising from the more covalent interactions of the network former oxide. The presence of glass modifier cations serves to slightly perturb the network vibrational frequencies through cation size effects. Alkali content correlates with the fraction of non-bridging oxygen atoms present in the glass and is manifested by marked changes in measured Raman spectra. These observations form a basis for application of this technique to framework structural studies of simple alkali silicate glasses.

The capability of Raman spectroscopy to discern silica and silicic acid rich regions in $Na_2O \cdot 3SiO_2$ glass fibers subjected to hydrothermal dissolutuion conditions will be discussed.

# LOW TEMPERATURE OXIDATION OF METALS AND SEMICONDUCTORS: THE ROLE OF NONCRYSTALLINE OXIDE FILMS

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The growth of oxide films on metals and semiconductors at low temperatures can be interpreted using the Cabrera-Mott theory. As a result, the oxides appear to be uniform in structure and lack paths of easy-ion movement.

Kinetic data taken from the literature have been introduced into the Ghez integration of the Cabrera-Mott equation. Values of activation energy for ion movement, the number of potentially mobile ions, and the self-induced voltage across the oxide have been derived. These values are compared with those obtained from other experiments and are found to correlate with a division of vitreous oxides into network formers and modifiers.

MOLECULES AS MODELS FOR BONDING IN SILICATES, AMINOSILICATES, THIOSILICATES AND GERMANATES

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Computational quantum chemistry is a powerful method for studying geometries, electron density distributions, reactions and energetics of small molecules. As the dimensions of SiOSi, SiNSi, SiSSi and GeOGe groups in gas phase molecules and solids are similar, the method can be used to explore potential surfaces and to generate deformation maps for a variety of molecules designed to mimic the local electronic structure of solid silicates, thiosilicates, aminosilicates and germanates. Optimized bridging bond lengths and angles obtained for these molecules conform with typical bond lengths and angles reported for the solids. Not only do the profiles of the potential energy curves conform with the ranges of bond lengths and angles observed for the solids, but they provide insight into the glass forming tendencies of $SiO_2$, $SiS_2$, $Si_3N_4$ and $GeO_2$. In addition, potential energy curves calculated for molecules with bridging SiOAl, SiOB, and SiOBe conform with the geometries observed for SiOT groups (T=B,Al,Be) in silicates.

# THE STRAINED MIXED CLUSTER MODEL OF THE GLASSY STATE

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The strained mixed cluster (SMC) model of the glassy state[1),2)] has been shown[3)] to be a viable alternative to the widely used Zachariasen-Warren (Z-W) model[4)]. Based on a phase diagram approach it can account in some detail for the observed properties of inorganic glasses, e.g. the occurrence of $T_g$, the enhanced glass stability near (but not at) eutectics, the occurrence of glass forming regions in parts of phase diagrams far from any conventionally accepted glass former, and the ability of some quartz analogues (e.g. $BPO_4$, $ZnP_2O_5$, but not $AlPO_4$) to form glasses. With it "glass former" and "non-bridging oxygen" are completely re-interpreted on a basis that is consistent with observations based on glass stability, and on physical measurements (e.g. NMR, XPCS etc.). The SMC model can also explain the behaviour of transition metals in glasses (of great importance for fibre optical communication); and the significance of small additions of impurity in stabilising commercial glasses, e.g. soda-lime-silica, against devitrification. A final advantage of the SMC model is that it can be used predictively, something not too readily achievable with Z-W.

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# ANNEALING OF RADIATION-INDUCED DEFECT CENTERS IN HIGH-PURITY BULK FUSED SILICAS BY MOLECULAR DIFFUSION MECHANISMS

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Electron spin resonance (ESR) has been used to characterize and quantify radiation induced defect centers in high purity fused silicas. It is rapidly becoming evident that production kinetics and thermal bleaching mechanisms are often dominated by molecular diffusion. Griscom et al[1] have shown that diffusion of radiolytic $H_2$ results in the bleaching of nonbridging-oxygen hole centers and the production of a metastable E' center variant above 200K in X-irradiated high-water silicas ($\gtrsim$ 1200 ppm OH). Edwards and Fowler[2] have suggested $O_2$ diffusion to account for the annealing of E' centers and coupled growth of peroxy radicals[3] near 450K in $\gamma$-irradiated low-water silicas ($\lesssim$ 5 ppm OH). The present paper proposes that diffusion of radiolytic $H_2O$ may be the rate determining mechanism for the thermal bleaching of E' centers near 600K in $\gamma$-irradiated high-water silicas. (Significantly, radiolytic water is inferred to be produced by ~ 1 MeV $\gamma$ rays but not by X rays of $\lesssim$ 100 keV). Isothermal and isochronal anneal data will be shown which can be fit by standard expressions for second-order kinetic processes in solids, utilizing published diffusion coefficients for $H_2O$ in silica. It appears that the processes elucidated here may also be active in the oxide layers of MOS device structures.[4]

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BORON COORDINATION IN RAPIDLY COOLED AND IN ANNEALED ALUMINOBOROSILICATE GLASS FIBER

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10$\mu$m diameter fiber was formed from a calcium aluminoborosilicate glass melt (mole%: 58.5 $SiO_2$, 9.5 $Al_2O_3$, 25 CaO, 5 $B_2O_3$) using the single crucible technique. Some of the fiber was annealed for 0.5 hr. at 948K. Refractive index (n), fraction of four coordinated borons ($N_4$) and the degree of crystallinity were measured in as formed and in annealed fibers. The results show:

| | As formed (approximately cooled at $10^5$K/sec.) | annealed |
|---|---|---|
| crystallinity | undetectable | undetectable |
| refractive index (at room temperature) | 1.557 | 1.562 |
| $N_4$ (%) | 10 | 16 |

These results show, for the first time, a change in B-coordination upon structural relaxation in an oxide glass.

The $N$ value in annealed fiber is much less than the value of 100% based on the simple notion that when the molar ratio $\frac{Al_2O_3+B_2O_3}{CaO}$ is less than unity, all borons are four-coordinated. A microscopic model will be presented to explain these observations.

# ELECTRONIC CONSEQUENCES OF THE SYMMETRIES IN COVALENT AMORPHOUS SEMICONDUCTORS*

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We examine the electronic consequences of idealized lattices that correctly model the fact that covalent amorphous solids contain regions with a high degree of local order. In its ideal form this order cannot be described by regular lattices in ordinary three dimensional space (crystals), but it is manifested by certain lattice structures ("polytopes") in positively curved non-euclidean three dimensional space.[1] We have previously studied such polytopes in two dimensional space[2] and have shown that these structures possess a symmetry quantum number k in analogy to the momentum quantum number of ordinary crystals. Using the "spherical torus" idea recently discussed by Sadoc and Mosseri,[3] we show that three dimensional polytopes which are representative of tetrahedrally coordinated solids also possess such a k quantum number. We present explicit calculations of the electronic states of a polytope containing 240 atoms using a realistic tight binding hamiltonian for Si. This approach may be viewed as a refinement of the use of the Bethe lattice in the study of the amorphous state. We demonstrate that the ideal curved space lattice has an indirect band gap just as crystal Si does. Therefore to the extent that the symmetries of the polytope are preserved in amorphous Si, approximate optical selection rules (e.g. $\Delta \vec{k} = 0$) apply. Experimental evidence for this point of view is contained in the literature in the pressure dependence of the absorption edge in a-Si.

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LOCAL ORDER IN AMORPHOUS GaAs, GaP AND $Ga_xSb_{1-x}$ COMPOUNDS BY ELECTRON DIFFRACTION, IN RELATION WITH ELECTRONIC PROPERTIES

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The atomic structure of flash-evaporated nearly-stoichiometric amorphous GaAs and GaP films and non-stoichiometric amorphous $Ga_xSb_{1-x}$ (x ranging from 0.48 to 0.31) films has been investigated by electron diffraction. Using a simple criterion on the relative peak positions of the interference functions (I(k)), it is demonstrated that the short-range order in all compound films is consistent with structure models with even-membered rings only (Connell-Temkin type). a-GaAs should be described by a relaxed C. T. model, while a-GaP and a-GaP and a-$Ga_xSb_{1-x}$ are better represented by an unrelaxed network; this last result can be attributed to the presence of defects such as wrong bonds. Radial distribution functions (RDF) have been derived from the diffraction patterns of the amorphous $Ga_xSb_{1-x}$ films, and the first-neighbour coordination numbers (CN) have been estimated. As long as the Sb nominal concentration does not exceed 54 percent, the C.N. values are consistent with a model in which the Sb atoms in excess would be incorporated into the amorphous tetracoordinated GaSb matrix with three-fold coordination. For larger derivations from stoichimetry, the influence of Sb-Sb bonds becomes prominent. For high Sb concentrations (69 percent) a drastic decrease of the CN value is observed, accompanied by a change of shape of the I(k) and RDF spectra. This indicates a profound modification of the film structure, which is discussed in terms of different models. An attempt to fit the experimental results quantitatively is given, using linear combinations of the I(k) and RDF of the different possible phases. The structure results as a function of composition for a-$Ga_xSb_{1-x}$ films are eventually discussed in relation with the optical and electrical properties determined on the same samples, which show a gradual modification with increasing Sb concentration. The data are analyzed in terms of chemical bonding and specific defects.

SEMIEMPIRICAL MOLECULAR ORBITAL STUDIES OF INTRINSIC DEFECTS IN a-$SiO_2$*

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The intrinsic point defects in a-$SiO_2$ have recently received considerable attention[1-3]. Careful use of paramagnetic resonance, coupled with annealing and optical studies, has led to unambiguous identification of three fundamental defects[1]. These are the E' center, the peroxy radical and the non-bridging oxygen hole center (NBOHC). Theoretical studies[2] of the first two defects have led to greater understanding of experiment through inclusion of lattice relaxation. Two models exist for the NBOHC. One, by Skuja and Silin[3], invokes a Jahn-Teller splitting to explain 2 eV optical transitions. The other, by Griscom[1], is an extension of a model devised for alkali silicate glasses and involves pairs of oxygens, one of which is adjacent to a proton. Using MOPN, a semiempirical spin unrestricted molecular orbital program, we have done molecular orbital studies of both NBOHC models. Our results support the Griscom model and not the Skuja-Silin model. These results, coupled with our earlier calculations[2] on the E' and peroxy defects, allow us to address defect formation and transformation processes in a logical way. In particular, these results are consistent with our speculations[2] on the sequential creation of NBOHC, peroxy precursor, and peroxy radical by hole trapping.

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# EFFECTS OF PRESSURE ON THERMAL STABILITY OF NONCRYSTALLINE SOLIDS

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The irreversible crystallization of transition metal-metalloid amorphous materials versus temperature has been well studied. However, the effect of elevated pressures on this transition has yet to be explored. Preliminary experiments, using energy dispersive x-ray diffraction techniques, indicate that pressures of about 2.0 GPa suppress crystallization, compared to ambient pressures.

Ribbons were placed between the anvils of a high temperature diamond-anvil cell and heated at a constant rate in the 400° to 500° C range. A synchrotron radiation source was used for rapid collection of structural data. Under zero load, the sample crystallized at about 450° C within the 10 minute spectrum collection time. However, when pressure was applied, the sample did not show evidence of crystallization up to more than 500° C, the present operating limit of our cells. The next series of experiments will provide more controlled heating to quantify the effect of pressure on crystallization versus temperature.

STRUCTURE AND PROPERTIES OF AMORPHOUS AND CRYSTALLINE ALKALI SILICATES

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The crystalline alkali silicates, $xM_2O(1-x)SiO_2$, represent an interesting gradation in structural type. At one end of the spectrum lies the open, directionally bonded, 3-dimensional framework structure of silica. At higher alkali contents atomic arrangements become increasingly dominated by the close-packed regions surrounding the M ions. Lithium metasilicate, for example, can be represented, to a good approximation, by a HCP oxygen sublattice with Si and Li atoms occupying tetrahedral interstices.

The contrasting properties of open, directionally bonded structures on the one hand and close-packed atoms interacting through central force fields on the other are investigated for a range of amorphous and crystalline silcates. Attention is focused on models which attempt to reproduce the composition - dependence of properties such as the radial distribution function, density, phonon density of states and phase sepation.

# STRUCTURE AND BONDING: SIMPLE MODELS FROM COMPLEX STRUCTURES

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We discuss the way the electronic properties affects the atomic structure of the crystalline or non crystalline arrays of atoms. Illustrating examples are choosen in the field of small aggregates, crystalline and amorphous structures.

Attention is focused on sp bonded systems. The total energy is computed in the tight binding picture as the sum of an (attractive) valence electron energy and an additional effective pair interaction repulsive potential. The total energy is minimized in order to obtain the most stable configuration at 0 K.

The growth sequence of small aggregates is first analyzed. For group IV elements, a special stability is found for the regular polyhedral structures (tetrahedron, cube, dodecahedron), with an additionnal Jahn-Teller deformation. Fivefold local axes are frequently found in small aggregates. Infinite systems (crystalline, amorphous and liquids) are considered. The stability of group IV, V and VI elements and their isoelectronic alloys is discussed. The 8-N rule is discussed. Special attention is paid to the pressure and temperature effects with a particular emphasis to liquid Si and Ge. In the latter case, the p bonding is found to play a particular role in the coordination ($Z \sim 6.5$) of liquid Si and Ge.

Endly the energy of some topological defects (disclination) is computed.

# THERMODYNAMIC AND STRUCTURAL INFERENCES FROM ACTIVITY MODELS IN SILICATES

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A new modeling approach is described for thermodynamic predictions of multicomponent, multiphase high temperature silicate systems including coal slags. The model, which attributes negative deviations from ideal solution behaviour to the formation of complex liquids and solids, is demonstrated for systems containing $K_2O$, $Na_2O$, $Al_2O_3$, CaO, and $SiO_2$. Good agreement between the model predictions and experimental vapor pressure data is found. Predictions concerning melting and phase composition are also given.

The basis of the present solution model is as follows. We attribute large negative deviations from ideal thermodynamic activity behaviour to the formation of stable complex liquids (and solids) such as $K_2SiO_3$, $KAlSiO_4$,... The free energies of formation ($\Delta G_f$) are either known or can be estimated for these component liquids (and solids). By minimizing the total system free energy one can calculate the equilibrium composition with respect to these components. Thus, for instance, the mole fraction of $K_2O$ present in equilibrium with $K_2SiO_3$, and other complex liquids (and solids) containing $K_2O$, is known. We have shown that the component activities can, to a good approximation, be equated to these mole fraction quantities. From this assumption of Ideal Mixing of Complex Phases (IMCP) it also follows that alkali partial pressures can be obtained.

We have tested the model by comparing predicted vapor pressure data determined in this manner with experimental values. The experimental partial pressure data were obtained by Knudsen effusion mass spectrometry. Thermodynamic activities and phase compositions are also calculated using this model.

# EFFECT OF STRUCTURE ON THE ELECTRICAL PROPERTIES OF CHALCOGENIDE GLASSES

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The effect of structure on the dc conductivity ($\sigma$) of chalcogenide glasses was first demonstrated on $As_2Te_3$ and $As_2Te_3Ge$ films. Films deposited at 77K display variable range hopping while annealing at 300K restores the exponential dependence of $\sigma$ on T commonly observed in bulk glasses. This behavior was explained in terms of creation of neutral defects in the low temperature films which are absent in bulk glasses where only charged defects are present. On the other hand, it was recently shown that $\sigma_{ac}$ in chalcogenide glasses was best explained by Elliott's theory. This theory assumes correlated barrier hopping (CBH) between both paired and random charged defect centers. Films are best described by CBH between random defects which results in $\sigma \propto \omega^s$ where s is temperature dependent and tends to unity with decreasing T, while CBH between paired defects applies to bulk glasses with s essentially temperature independent and equal to unity. Elliott's theory was confirmed by measurements of $\sigma_{ac}$ down to 4.2K on $As_2Te_3$, $As_2Te_3Ge$ and $SiO_2$ films deposited at 77K. The only discrepancy with theory is that the temperature dependence on the as-deposited films is much weaker than theoretically predicted. This discrepancy is removed by assuming that even as-deposited films contain a small amount (10%) of paired defects. Finally, the best way to link structure and electrical properties is to study known glass formers, e.g. $GeSe_2$ and $As_2Se_3$. The as-deposited films display the same temperature dependence observed on $As_2Te_3$. But in contrast with the tellurides the temperature dependence remains unchanged by annealing at 300K. One must anneal above the glass temperature (500K for $GeSe_2$) to obtain a temperature independent conductivity.

# THE NATURE OF GLASS FAILURE AND VISCOUS FLOW IN COMPUTER SIMULATION STUDIES

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In previous studies, the rheological properties and failure of systems of interacting atoms representing silicate glasses in computer simulations was demonstrated. Figures showing glass flow after an induced strain and the failure of simulated ensembles when the system of atoms was extended are reviewed. In this talk we discuss further the nature of failure and viscous flow.

When systems of around two thousand atoms representing sodium silicate glass and silica glass are expanded in molecular dynamic simulation experiments, they are found to break at stresses comparable to although somewhat higher than currently observed strengths of real high strength fibers, namely, 1 and 2.4 million psi, for the sodium silicate and silica glasses respectively. The simulated systems fail or break at stresses which are many times less than the maximum stress of the Si-O bond. Therefore stress concentration must occur with only some of the Si-O bonds being stretched to the maximum restoring force before separation. Since there are no existing flaws or heterogeneities other than those due to the randomness in the atomic structure, stress concentration must be of a statistical nature. By looking at the virial on each atom, the development of stress concentration is observed and one can find which bonds experience the maximum restoring force during the course of the extension and failure.

Viscous flow similarly depends on Si-O bonds being stretched beyond their maximum restoring force. Network ion diffusion and therefore viscosity correlates with the formation of non-bridging oxygen atoms in the structure. However, the activation energy for the formation of non-bridging oxygen atoms is around 40 kcal/mole while that for diffusion is around 140 kcal/mole. This suggests a mechanism in which more than one non-bridging oxygen atom participates in a topological network change. A mechanism for viscous flow is proposed and compared with other proposed mechanisms.

# NEAREST NEIGHBOR ENVIRONMENT IN COVALENTLY BONDED NONCRYSTALLINE SOLIDS

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The extended x-ray absorption fine structure (EXAFS) technique is particularly suited for determining the nearest neighbor environment. Ideally EXAFS can determine the numbers, types, average distances and disorder about that average of the first coordination shell of atoms. EXAFS has been applied to study amorphous Ge and its hydrogenated form and to some ternary tetrahedrally bonded alloys. The striking results of these studies are the rigidity of the covalent bond length. To within a few thousands of an Angstrom the Ge-Ge bond remains the same in the crystalline and its various amorphous forms. In the ternary alloys $(Ga_xIn_{1-x})As$ and $(Ga_xIn_{1-x})Sb$, the Ga and In atoms are placed in a disordered fashion on their sublattice. Although x-ray diffraction results show an almost linear variation of lattice constant with composition, the EXAFS results show that Ga-Sb, In-Sb, Ga-As and In-As bond lengths change much less with composition than expected from the lattice variation in agreement with other measurements.[1] Experimental evidence whether the rigidity of the covalent bond distance is caused by clustering of the binary compounds in the alloys or not will be presented.

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CHARACTERISTIC TEMPERATURE AND MIDDLE RANGE DISORDER OF GLASSFORMING COMPOUNDS

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In order to obtain informations about bonding nature in glasses, the heat capacity data of silicate, borate, germanate and phosphate glasses were analyzed by using the three band theory. This theory assumes that heat capacity of glass can be represented by three characteristic temperatures $\Theta_E$, $\Theta_1$ and $\Theta_3$ which reflect the independent Einstein-type vibrations of modifying cations, the interatomic one-dimensional vibrations of network forming ions and the intermolecular three-dimensional vibrations of glass networks, respectively. The data of silicate compounds were also analyzed on the same assumption. The values of $\Theta_E$ were found to be dependent on the kind of alkali ions but independent of alkali content and the kind of network formers. They were slightly lower than those obtained for crystals having the same composition. The values of $\Theta_1$ seemed to reflect the bond strength of B-O, Si-O, Ge-O and P-O in glass structure and decreased with increasing alkali content, indicating the weakening of bond strength. However, $\Theta_1$ increased when the coordination number of B or Ge increased. The values of $\Theta_3$ for silicate, borate, germanate and phosphate glasses varied depending upon their compositions. The glasses containing low contents of network modifiers were particularly smaller than those of comparable crystals. These data were used to discuss the randomness or medium range disorder in glass structure.

STRUCTURAL SIMULATION OF
METALLIC GLASSES: $Cu_xZr_{1-x}$*

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ABSTRACT

The atomic-scale structures of binary metallic glasses $Cu_xZr_{1-x}$ for x values range from 0.2 to 0.8 are studied by computer simulation. Large number of metallic atoms are initially randomly positioned in a cubic box whose dimension commensurates with the mass density of the metallic glass. The atoms are allowed to interact via a pair-wise Leonard-Jones type of potential with periodic boundary condition imposed. The parameters for the interacting potentials are extracted from the relevant experimental data. The atoms are sequentially moved to new positions of zero force field until the total energy of the structure stabilizes to one part in $10^8$. Both zero temperature quenching and Monte-Carlo type of finite temperature quenching are tested in the relaxation process; the later is found to have much faster convergence. The models are analyzed by computing the total and the partial pair correlation functions and the short-range chemical order parameters and by studying their dependence on the compositional parameter x. Application of these models to the electronic structure calculation of metallic glasses from the first-principles will also be discussed.

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STRUCTURAL IMPLICATIONS OF GAS TRANSPORT IN AMORPHOUS SOLIDS

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The interstitial structure of vitreous silica and related materials is in a difficult size range for evaluation. Diffraction and spectroscopic techniques are generally limited to more local structural descriptions (bond lengths, coordination numbers, defect structures, etc.). Electron microscopy surveys somewhat larger geometry (e.g., phase separation). A careful analysis of the diffusion and solubility of inert gas atoms and molecules provides an experimental probe for interstitial structure.[1] Such information is of substantial interest because of the basis for structural classification (in the manner of Bernal's canonical hole model[2] of liquid structure). There is also a close connection to some commercially important processes, such as the thermal oxidation of silicon.[3]

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# OPTICAL AND STRUCTURAL PROPERTIES OF ZIRCONIUM FLUORIDE GLASSES

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A new class of glasses based on the $ZrF_4$-$BaF_2$-$LaF_3$ ternary system has recently been developed by Poulain et al[1] at the University of Rennes. These materials are potentially attractive for a variety of applications including infrared windows, thin glass films and sealants, laser hosts and low loss waveguides. In the latter context, fluoride glasses appear capable of offering optical transparency several orders of magnitude beyond present day silica based waveguides.[2,3] Structural information on many of these new glasses is rather sparse. This paper will attempt to provide an overview of the present state of knowledge of fluoride glasses while at the same time summarizing recent developments in the applications areas. The role of trace oxygen and water in these glasses appears to be very significant. Recent Raman and infrared absorption spectra relative to this problem will be reviewed.

An important structural problem in fluoride glasses relates to glass stability and the potential nucleation and growth of crystallites during melting, casting and fiber drawing operations. Projected high transparencies of this class of materials hinge critically on a Rayleigh scattering model with $\lambda^{-4}$ dependence. The validity of this assumption has been in question for the fluoride glass system. Recent work to synthesize extremely homogeneous, low scattering level fluoride glasses will be discussed.[4] The data obtained on these materials will be compared with the response expected from a pure Rayleigh scatterer. In addition, the typical crystallization behavior in the zirconium fluoride glass system will be described along with the constraints which such behavior places on glass melting and fiber drawing.

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# SPECTROSCOPIC STUDIES OF MIXED ALKALI GLASSES

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Spectroscopic studies of series of mixed alkali glasses, represented by $xM_2O(1-x)M'_2O \cdot yA_pO_q$ (where $M_2O$ and $M'_2O$ are alkali oxides and $A_pO_q$ is a network former), systematically employ the key compositional variable x to investigate the structure, bonding, and ionic interactions of ionic oxide glasses. Such glasses are well known to exhibit important variations in their physical properties as x varies, including extrema in transport properties and unusual behavior of mechanical loss. The Raman, far infrared and Brillouin spectra of mixed alkali silicate glasses will be presented and analyzed to help develop an interpretation of these effects based on determination of cation-motion frequencies and interionic forces, ion-distribution and network-structural features. The spectra of network-isotopically substituted $B_2O_3$-based glasses will be presented to elucidate the effect of the introduction of cations and cation mixtures.

The study of mixed alkali glasses not only helps elucidate their properties it also provides a method for addressing certain annealing, or thermal relaxation processes, because varying x forces the introduction of intrinsic (unannealable) molecular scale strain which can be of the same type and have the same spectral manifestations as those characteristic of but annealable from single alkali glasses. The variation of local structure and strain with variation of alkali (via mixed alkali series) and with variation of thermal treatment, studied by Raman and far infrared methods, will be presented through comparisons of the spectra of annealed and unannealed single alkali and mixed alkali silicate glasses.

This work was supported in part by the Office of Naval Research. Partial support and use of the facilities of the Materials Science Program at Brown University is acknowledged.

# AN $^{18}O$ STUDY OF THE OXIDATION MECHANISM OF SILICON IN DRY OXYGEN

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The mechanism of thermal oxidation of silicon in dry oxygen was studied using $^{18}O$ as a tracer. $SiO_2$ layers first grown in natural oxygen were further grown in $^{18}O$ enriched oxygen. We have previously shown that for oxide films of thicknesses higher than 1300 Å, the oxide growth occurs essentially by a mechanism of migration of oxygen through the whole oxide without any interaction with the network and then reaction with silicon near the $Si/SiO_2$ interface.

The aim of this work is to determine : (i) the possible origins of $^{18}O$ fixation near the external surface of the oxide ($^{18}O$ FNES) and (ii) the possible growth mechanisms of films of thicknesses ranging from 2600 Å down to 50 Å. It was shown that $^{18}O$ FNES does not seem to be due to some interfering phenomena (network oxygen exchange with water vapor traces or effects connected with the experimental procedure) and is not due to other growth mechanism by Si transport. A step by step motion of network oxygen atoms seems to be the more likely to explain $^{18}O$ FNES. The amount of $^{18}O$ FNES is all the more important as the original thickness of the film is smaller. Even for thicknesses under 200 Å, we always found high amounts of $^{18}O$ fixed near the $Si/SiO_2$ interface, However the amount of $^{18}O$ FNES can reach 50 % of the total amount of $^{18}O$ for $\sim$ 50 Å thickness films.

Results are discussed considering possible structural modifications at the beginning of growth.

# NEW WAYS OF SILICON OXIDATION BY LOW ENERGY OXYGEN IONS AND UNDER ELECTRON BOMBARDMENT. STUDY OF GROWTH MECHANISMS AND STRUCTURE

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## ABSTRACT

We have studied oxidation of silicon by low energy (100 eV) and high intensity ($\sim$ 1mA/cm$^2$) oxygen ion beams ($O_2^+$ and $O^+$ or $O^-$, $O_2^-$ and electrons) and at a low oxygen pressure ($p_{O_2} \sim 10^{-3}$ Torr) under electron bombardment at 100 eV.

It was shown that oxide films formed by positive ion beams reached rapidly a constant thickness ($\sim$ 60 Å) for a substrate temperature ranging from 27 to 500°C, suggesting important competitive sputtering phenomenon (for one thing, from $Ar^+$ component).

For oxide films formed by negative species beam ($O^-$, $O_2^-$ and electrons) the thickness is also limited to about 25 Å, at room temperature.

Thicker films are obtained with a low oxygen pressure ($\sim 10^{-3}$ Torr) under electron bombardment : thickness increases with time ; for a 45 minutes oxidation time, the thickness varies from 400 Å to 2200 Å when the substrate temperature increases from 600 to 800°C. An oxide layer was first grown in $^{16}O_2$ and then further grown in $^{18}O_2$ enriched oxygen at 800°C. $^{18}O$ is located only near the surface of the oxide in contrast with thermal oxidation.

Growth mechanism will be discussed considering structural defects and caracteristics.

STRUCTURE AND BONDING IN COVALENT NONCRYSTALLINE SOLIDS

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The usual description of noncrystalline (NC) solids in terms of continuous random network (CRN) models associated with radial distibution functions (RDF) appears to be insufficient for covalent NC solids as the possible perfection of the highly directional chemical bonds, correlation between bond angles and lengths, and the extent of localized ordering are generally not adequately taken into account. For example, the relationship between the crystalline and NC forms is quite different for $SiO_2$ than for Si even though the short-range-order in the NC forms (as indicated by the RDFs) is similar. As a result of bonding perfection, the bonding electrons in v-$SiO_2$ are apparently highly delocalized, despite the lack of long-range-order. Also, bond lengths and angles are correlated rather than random because they are determined by the actual local hybridization state. Various features of v-$SiO_2$ can be interpreted if the distributions of Si-O bond lengths, Si-O-Si bond angles, $\phi$, and the torsional angles (by which two $SiO_{4}/_{2}$ tetrahedra are rotated with respect to each other) are considered as non-random. The small variation in bond energy ($\tilde{}2$ kcal $mole^{-1}$) as $\phi$ varies from 120° to 180° in v-$SiO_2$ indicates that the Si-O bond is very flexible; this feature is primarily responsible for the high degree of bond ordering, and for the occurrence of ordered regions. The latter behavior is particularly exhibited by the diffusion of $O_2$ molecules in thermally grown v-$SiO_2$ films on silicon. Depending on growth and/or heat treatment conditions, the diffusivity of $O_2$ molecules in these films can be 2-3 orders of magnitude higher than in fused v-$SiO_2$ and exhibits a dependence on the crystallographic orientation of the Si substrate (quasi-epitaxy). This behavior is attributed to the presence of structural channels where the atomic arrangement is similar to that along the C-axis in tridymite crystal.

LOCAL STRUCTURE AROUND GERMANIUM OR MODIFIER COMPONENT IN OXIDE GLASSES USING X-RAY SPECTROSCOPY

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X-ray absorption spectroscopy in its two aspects, XANES (near edge structure) and EXAFS, can be used to study the local structure around a chosen element in glasses; it is a method of choice because of its atomic selectivity whatever the crystalline or amorphous state. The absorbing atom can be a forming element or a modifier component of the glass. Relative to forming elements, studies are made, in our group, about Ge environment in binary and multi-component glasses; the rigidity of the $GeO_4$ tetrahedron is generally observed through small variations of Ge-O distance are measured. These variations associated with the presence or not, in EXAFS spectra, of a contribution from the second atomic shell give information about the changes in local structure and the maintenance of a three dimensional order in some cases. The complementarity of EXAFS and XANES information is especially interesting for modifier components. We investigate, by that way, the state and environment of 3d-elements intervening as a major or minor component, principally in silicate glasses. Taking into account the complexity of the edge structure, we chose a pragmatic approach, making comparisons between many crystalline compounds where the crystallochemistry of the d-element is well-known. On the other hand, EXAFS analysis at the metal K-edge informs about the first neighbor atomic shell, confirming generally that it is rather well ordered with shorter distances than in the corresponding crystals. As for the forming elements the presence of a further atomic shell contribution is a very important information. Discussion is presented about that point in some dilute or concentrated systems and also concerning the reorganization during the glass to crystal transition.

# TOPOLOGICAL STRUCTURE OF NETWORK GLASSES

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Inorganic network glasses fall into three broad classes: borates, silicates and ...ogenide alloys. Topology provides a virtually exact description of the glass-...ing tendency[1] and molecular structure[2] of chalcogenide alloy glasses as ...tions of continuously variable composition. By extending this mean-field-like ...y to specific structures I have successfully determined cluster morphologies ...stable and metastable microphases for several specific binary and ternary alloys ...nctions of composition. The theory has successfully guided and accelerated ...development of Raman[3] and Mössbauer[4] studies of the molecular structure. It ...stimulated the discovery of and explained microscopically the new phenomena ...versible crystallization,[5] periodic photodarkening and bleaching,[6] induced ...l anisotropy,[7] and giant photocontraction.[8] The molecular structure of oxide ... is determined by similar topological considerations which are modified ...ly because of the very low enthalpy of formation of non-bridging oxygens. ...s of spectroscopic data shows that the standard model for $g$-$SiO_2$, the ...uous random network, is incorrect. The correct model involves ...talline clusters with the interior morphology of cristobalite, whose surfaces ...ered by non-bridging oxygens. The diameters of the clusters are about ...nd the number of non-bridging oxygens is about 10% of the total number.

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Transient Luminescence, Transport and Photoconductivity in Chalcogenide Glasses and Amorphous $SiO_2$

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Abstract

The chalcogenide glasses are perhaps the most thoroughly studied amorphous semiconductor systems. In the past two decades their measured properties have been repeatedly compared with model predictions and served as guides in the search for fundamental concepts and principles necessary for amorphous semiconductors. An example is the synthesis of the Mott-CFO model which is a low carrier density and high carrier mobility picture that involves the concepts of band tail states and mobility edge. On the other hand, Emin proposed that the charged carriers in chalcogenide glasses form small polarons and necessarily implies low carrier mobility because of small band width caused by atomic displacements associated with self-trapping. The small-polaron model can explain, in addition, the Hall effect sign anomaly and the difference in activation between the Peltier heat and conductivity. In spite of the fact that the Mott-CFO model and the small-polaron model are orthogonal to each other, the experimental data prior to 1978 have not been able to discriminate which is the correct model. In this work, transient optical and transport data which have rapidly accumulated since 1979 are considered. These recent data enable us to narrow down the possible states that can exist in chalcogenide glasses. As a result of this analysis, a minimal set of states has been proposed that can explain the totality of optical and transport data. It confirms that transport occurs by small polaron hopping. The proposed minimum set of states is consistent with Anderson's bipolaronic ground state. The transient transport data, transient optical data, the dynamical dielectric relaxation data, and the volume and enthalpy recovery data of chalcogenide glasses are shown to conform to a universal pattern predicted by a recent unified model of relaxation at low frequencies/long times of condensed matter in general.

INTERATOMIC POTENTIALS FOR INSULATING SOLIDS

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Simulation of the static and dynamic properties of amorphous materials requires an accurate knowledge of interatomic potentials. These should be physically reasonable and, as far as possible transferable from one material to another.

Interatomic potentials suitable for use in insulating solids such as silicate glasses have been derived. These have been obtained from analysis of the results of detailed ab initio molecular orbital calculations. The calculations were performed on molecules and groups of molecules chosen to simulate the environments and interactions of atoms in crystals. Particular attention has been payed to non-bonded (next-nearest neighbor) short range forces and to the importance of three body (angle-bending) forces.

# THE CALCULATION OF SOME OPTICAL PARAMETERS

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The formalism of Wemple[1,2] is used to calculate the material dispersion zero wavelength $\lambda_o$ where $d^2n/d\lambda^2 = 0$, n being the refractive index, and the material dispersion slope $dM/d\lambda = (\lambda/c)\ (d^3n/d\lambda^3)$ at $\lambda_o$, where c is the velocity of light. These parameters are important for the design of glasses for use in optical waveguides. Calculated values are found to be within 20% for $\lambda_o$ and within a factor of three for $dM/d\lambda$, both for crystals and glasses.

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THERMODYNAMICS, STRUCTURE, AND BONDING IN FRAMEWORK SILICATE AND ALUMINOSILICATE GLASSES

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Structural studies (Raman spectra and x-ray scattering) suggest that glasses of the type $SiO_2$-$M^{n+}_{1/n}AlO_2$ consist of three dimensional aluminosilicate framework with the M cations in large interstitial "stuffing" sites. The thermodynamics of mixing in these glasses reflect three factors: the strength of interaction between $M^{n+}$ and $O^{=}$ and its effect in perturbing the tetrahedral framework, the size of the cation, and a stabilization near the 50 mole % composition probably due to polarization of T-O-T bonds rather than to aluminum avoidance. Tendencies toward immiscibility and trends in the enthalpy of vitrification also reflect these bonding factors. Some recent calorimetric studies on these glasses will be discussed. These findings will be correlated with some predictions of bond lengths, angles, and energies made by molecular orbital theory.

CURVED SPACE APPROACH TO THE
RELATION BETWEEN LONG RANGE DISORDER
AND LOCAL ORDER IN
AMORPHOUS TETRACOORDINATED SEMICONDUCTORS

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From a geometrical point of view, the lack of periodicity in amorphous systems is due to the presence of a rather well defined local order uncompatible with crystalline 3D periodicity in the euclidean space. As a first step we let the local order extend in a freely (positively) curved space where the tiling becomes perfect. The second step consists in lowering the curvature to recover a realistic "euclidean" structure. This is achieved by introducing defects of different dimensionality (disclination lines, internal surfaces) which always introduce elastic distortion. We present in addition a comparison between the cohesive properties of some of these structures (both "ideal" and with defects) which differ by the choice of the local order. This is done in a simple tight binding framework which is very sensitive to connectivity effects and does not take into account elastic strains.

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# Radial Distribution Functions for the Amorphous Metals Fe-W (72 at.% Fe) and Ni-P (75 at.% Ni) at High Pressure

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Radial distribution functions for two amorphous metals, Fe-W (72 at.% Fe) and Ni-P (75 at.% Ni), contained at high pressure in a diamond anvil pressure cell, are discussed. The experimental and computational procedures, the accuracy, and the general results are discussed for x-ray diffraction measurements made at room temperature and at pressures of 0, 0.3, 3.6, 7.5, and 10.5 GPa for the Fe-W sample, and at 0.15, 2.80, and 5.50 GPa for the Ni-P sample. The results indicate that the Fe-W material has an isothermal bulk modulus of about 170 GPa at room temperature and that the Ni-P material has a bulk modulus of about 370 GPa.

# POLYACETYLENE, $(CH)_x$: THE PROTOTYPE CONDUCTING POLYMER

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When silvery films of the flexible, semiconducting polymer, "polyacetylene," $(CH)_x$ are exposed to bromine, iodine, $AsF_5$, $H_2SO_4$, etc. vapor, they become "doped" with the species and are converted to p-type semiconductors. Their conductivity increases rapidly (over twelve orders of magnitude in certain cases) as doping proceeds. At ca. 0.02% dopant concentration, they undergo a pseudo semiconductor-metal transition and are converted to silvery, flexible films of "organic metals." At ca. 7% dopant concentration, they begin to exhibit significant Pauli susceptibility. They then possess all electronic and magnetic features characteristic of a conventional metal. When partly aligned trans-$(CH)_x$ films are treated with, e.g., $AsF_5$ to give compositions such as $[CH(AsF_5)_{0.1}]_x$, remarkably high conductivities (in excess of 2000 $ohm^{-1}cm^{-1}$ at room temperature) are obtained. The films may also be n-doped to give highly conducting materials such as $[(CH)Na_{0.1}]_x$, etc. Films of $(CH)_x$ may be electrochemically oxidized or reduced i.e. "doped" p-or n-type. This permits the use of $(CH)_x$ as the anode and cathode active material in the fabrication of lightweight, high power density, rechargeable "organic batteries." A qualitative description of the "soliton" concept of doping and conductivity in $(CH)_x$ will be given together with corresponding band diagrams.

# ELECTRIC TRANSPORT AND PHOTOCONDUCTIVITY IN NON-CRYSTALLINE FILMS

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Over the last few years considerable progress has been made in the study of electronic transport and photoconductivity in a wide range of amorphous materials. These embrace chalcogenides such as a-Se and a-$AS_2Se_3$, tetrahedrally bonded materials such as hydrogenated a-Si and organic systems such as molecularly-doped polymers. This talk will be concerned with a comparative survey of selected phenomena in these three classes of amorphous solids. The unifying theme is the role of localized states and how they influence and control photoelectronic processes such as electronic transport, photogeneration and their sensitivity to doping. Despite similarities, however, features are observed which are unique to each class and reflect their specific chemical nature.

INVESTIGATION OF THE "GLASSY" PROPERTIES OF NEUTRON AND ELECTRON IRRADIATED CRYSTALLINE QUARTZ RELATED TO THE ANOMALOUS LOW TEMPERATURE DYNAMICS OF NON-CRYSTALLINE SOLIDS.

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At low temperatures, non-crystalline solids exhibit dynamic properties which are unexpectedly different from these in crystals (linear specific heat, $T^2$ thermal conductivity, saturation of the ultrasonic absorption, etc). These "anomalies" are accounted for by the existence of configurational tunneling states present in addition to phonons. The microscopic origin of the tunneling centers, often described as two level systems (TLS), is however not known yet.

Another approach to the study of the TLS was introduced through the investigation of slightly fast neutron irradiated crystalline $SiO_2$, in which the 9 GHz hypersonic attenuation was found to be non-linear, similar to previous findings in different non-crystalline solids.[1] Until now different dynamical studies were carried out in neutron irradiated quartz and it turned out that the density of states of the TLS can be altered in a controlled way by changing the dose of the irradiating particles. High energy electron irradiation was found to cause similar "anomalies" although electrons are expected to cause simpler defects than neutrons, since displacement cascades are unlikely. Related damage studies as diffuse X-ray scattering, magnetic susceptibility and positron-annihilation lifetime studies were also carried out. The paramagnetic center production was found not to correlate directly with the density of states of the TLS, neither do the positron annihilation lifetime data; diffuse X-ray scattering studies give evidence for "amorphized" clusters in neutron but not in electron irradiated quartz.

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PENTACOORDINATE SILICON IN SILICATE MELTS, GLASSES AND AQUEOUS SOLUTIONS - CRYSTALLOGRAPHIC SUPPORT

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In general, silicon is coordinated by either four or six oxygen atoms. Including ligands other than silicon (N, C, F, Cl) into consideration $[SiA_5]$ groups have been proved to exist by crystal structure analyses in about 15 compounds. In all of them the $[SiA_5]$ polyhedra can be described as more or less distorted trigonal bipyramids. Stereochemical analysis of these polyhedra reveales that each of them can be considered to be a member of a series of continuous transition states between an ideal $[SiA_4]$ tetrahedron in a hexagonal close-packed array of A atoms and an ideal $[SiA_5]$ trigonal bipyramid.

Following Dunitz' reaction-path concept it is suggested that this observation reflects the atomistic mechanism taking place during reactions of silicates. For example, hydrolysis of a $\geq$Si-O-Si$\leq$ group in dissolved as well as in solid silicates involves occupation by an $OH^-$ ion of what is to become an apical position of a trigonal bipyramid of a $[SiO_5]$ intermediate and subsequent breakage of the Si-O-Si bond. Corresponding mechanisms are suggested for silicic acid condensation in solution and for dynamic processes in silicate melts. Since the average lifetime of $[SiO_5]$ intermediates should increase with pressure, reaction rates of silicates in water, melts and glasses should pass a maximum when the lifetime of $[SiO_4]$ and $[SiO_5]$ become comparable. It is suggested that non-negligible amounts of $[SiA_5]$ groups can be present in silicate glasses containing highly electronegative elements (H,P,C,N,Cl,F).

DIELECTRIC RESPONSE OF DISORDERED MATERIALS

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Two types of disorder are distinguished - structural disorder of the lattice leading ultimately to an amorphous solid, and positional or orientational disorder of point-like defects, e.g. electronic or ionic charges or molecular dipoles embedded in an otherwise "perfect" crystalline medium. Either type defies exact analytical specification and this renders conventional analytical treatments very difficult. In thc case of electrical transport, the discrete value of the steady state or dc conductivity may plausibly be approximated by a suitable choice or disposable parameters, but the theoretical fitting of the alternating current conductivity, $\sigma(\omega)$ , with its wide range of the expermentally available frequency $\omega$ , is effectively impossible with any degree of plausibility.

It is therefore noteworthy that the "universal" form of frequency dependence $\sigma(\omega) \propto \omega^n$ , with $0.6 < n < 1$ , is well accounted for in the many-body theory of dielectric polarisation which is applicable to all systems with random distribution of orientations of dipoles or positions of hopping charge carriers. The exponent $n$ is sensitive to local order and therefore to temperature, but the general form of the power law is not.

Measurements of ac conductivity have been reported on a wide range of materials and the presence of power-law behaviour was taken as "proof" of the presence of hopping electronic conduction. We point out that in many of these materials the dominant process may be dipolar polarisation and not hopping electronic conduction.

The values of the exponent $n$ fall in some charge carrier systems close to zero, corresponding to "strong low-frequency dispersion" in dielectric terms, and the significance of this phenomenon will be discussed.

# MAGIC-ANGLE SPINNING NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF SILICATE GLASSES

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High-resolution Nuclear Magnetic Resonance Spectroscopy of solids using "magic-angle spinning" methods is a new and potentially powerful tool for examining glass structure. Presently available methods allow us to examine the structural environment of Si, Al, B, O, and Na in glasses. At the Conference on Structure and Bonding in Noncrystalline Solids we will present data for silica and feldspar glasses and glasses in the system $CaO-MgO-SiO_2$. These results indicate that the nearest-neighbor and next-nearest-neighbor environments are very similar in crystals and glasses of the same composition and that the glasses become depolymerized as silica content decreases. The range of Si-O bond lengths in $SiO_2$ glass is about 0.01Å. The results are in good agreement with those of Raman spectroscopy and X-ray diffraction.

# IMPORTANCE OF NONCRYSTALLINE SILICON DIOXIDE FILMS IN THE SURVIVABILITY OF MODERN ELECTRONICS

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The operation of MOS and oxide-isolated bipolar VLSI circuits depends acutely on the electrical properties of silicon dioxide films, thermally grown, as well as chemically deposited. Performance over life, as well as survivability to various severe environments, such as high temperature and radiation, depends on both the bulk and interfacial properties of the silicon dioxide/silicon structures indigenous to nearly all high density integrated circuits. Electronic trapping in silicon dioxide films influences reliability on scaled devices where hot electronic carriers are uncontrollably injected from active semiconductor regions into the oxide films. Furthermore, radiation-induced electrons and holes are trapped in oxide regions at various rates depending on the applied fields and geometrics involved. The degree of electronic trapping in silicon dioxide films for these cases depends greatly on fabrication processing details. The diffusion of fabrication-related impurities, such as nitrogen and hydrogen, through the noncrystalline oxide films strongly influences the oxide trapping characteristics. The trapping characteristics for oxide films, possessing differences in impurity transport properties, will be presented and discussed for various technology types, such as CMOS and NMOS.

ABOUT GENERAL RELATIONSHIP BETWEEN STRUCTURE, PROPERTIES AND STABILITY IN SOME AMORPHOUS METALLIC ALLOYS

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A number of amorphous metallic binary alloys have been obtained using a vapour quenching technique and most of their basic properties have been measured including forming ability compositional range, stability against crystallization, structural information, electrical transport and magnetic behaviour. Some general features about alloying in the amorphous state have been strongly suggested by the data.

1) Forming ability

Binary metallic alloys are not obtained in the amorphous state when their composition corresponds to that of crystalline phases having either relatively small unit cells or no chemical order (or both).

2) Stability

The compositional dependence of the crystallization temperature is mostly determined by the liquidus slope of the corresponding equilibrium phase diagramme but some limitations come from structural effects.

3) Structure and short range chemical order

Both structural and chemical short range orders are very similar in crystalline, liquid and amorphous phases of a given binary metallic system. Differences have to be sought at medium distance level (and of course long range order level as long as crystals are concerned). Experimental evidence are given by NMR data in LaGa, MoB, NiB, CoB or CoP amorphous alloys, Mössbauer spectroscopy and/or diffraction data in EuAu, EuAl, AuSi, TMSn (TM = Cr, Mn, Fe, Co, Ni, Cu) amorphous alloys.

Some kind of "amorphous phase diagramme" can be proposed with quite the same occurrence to those observed in the classical equilibrium phase diagrammes = (i) Homogeneous solid solutions that is no chemical order with only one topological SRO whatever the alloy composition ($Si_xSn_{1-x}$, $0.2 < x < 0.8$) or with a structural change at a given composition ($Fe_xAu_{1-x}$, $Fe_xSi_{1-x}$), (ii) Heterogeneous multiphase systems, the amorphous alloy being a mixture of two (or more) well defined amorphous phases (composition and structure) whose proportions are determined by the average composition ($Co_{1-x}B_x$ which is a mixture of a CoB solid solution, a $Co_2B$ phase and an eutectic composition phase; $Au_xSi_{1-x}$ which is a mixture of SiAu interstitial solid solution and a $Au_3Si$ phase) (iii) "Intermediary" compounds with well defined structure and composition, and possibility of extended forming ability range thanks to "structural vacancies" (for instance $Fe_xSn_{1-x}$ amorphous alloys correspond to an amorphous $Fe_2Sn$ phase with vacancies either on the Fe or the Sn "network" to accommodate compositional changes from $x \simeq 0.1$ to $x \simeq 0.8$). Physical properties can be understood in the frame of these considerations (for instance magnetic properties of a $Fe_xSn_{1-x}$ or a $Co_xSn_{1-x}$).

POSSIBLE ROLE OF HYDROGEN FOR STABILIZATION OF THE AMORPHOUS SILICON STRUCTURE

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We have found that rf-sputteing in $H_2$ atmosphere produces films composed of microcrystalline hydrogenated Si (μc-Si:H) at substrate temperatures as low as ~30°C---the size of the microcrystals ranging from ~500 Å to ~50 Å in diameter, and also it is possible to obtain amorphous films. The μc-films thus produced show several interesting features. One of them is infra-red (IR) property. IR spectra from bonding between Si and H in μc-Si:H exhibit far clearer structure than those from amorphous films. In addition, SiH monohydride configurations responsible to stretching near 1990 $cm^{-1}$ is completely absent in the μc-films. So, it was easy to assign stretching vibration due to $(SiH_2)_n$ (n=1,2), $-SiH_3$ configurations and their combinations as reported already.[1,2]

In our paper, we would like to discuss the active role of SiH bonding for stabilizing the amorphous phase. The discussion is made on the basis of our study on thus fabricated microcrystalline and amorphous films as a function of fabrication conditions using variety of observation techniques such as high resolution transmission electron microscope, high sensitive Fourier transform IR spectrometry and so on.

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# GRADUAL LOSS OF CRYSTALLINE ORDER UNDER IRRADIATION: THE RADIOLYTIC METAMICT TRANSFORMATION OF $\alpha$-QUARTZ

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The transformation between crystalline and non-crystalline states of $SiO_2$ most commonly addressed is the devitrification of vitreous $SiO_2$ which provides a sharp interface between crystalline and non-crystalline phases but little information about non-crystalline structure [1]. A potentially more revealing sequence is the crystalline → non-crystalline transformation to the geological metamict state under irradiation. This transformation can be effected by neutron irradiation or heavy-ion recoil during $\alpha$ emission, but a more controlled approach is to utilize the radiolytic response of $SiO_2$ to ionizing radiation which effects the transformation through a step-by-step destabilization of Si-O-Si linkages [2]. It is suggested that this process imparts increased topological freedom to the connected network of $[SiO_4]$ tetrahedra which at a critical density of broken linkages subsequently rotate and rebond.

We have studied the radiolytic transformation of $\alpha$-quartz experimentally using the ionizing component of high-energy electron irradiation in the transmission electron microscope in an attempt to characterize a well-defined non-crystalline state of $SiO_2$ through the details of how it is formed. The transition zone has been investigated in near-atomic detail using high-resolution structure image projections and convergent-beam electron diffraction. The results suggest that progressive disorder evolves from local stochastic rearrangements of individual $[SiO_4]$ coordination units; however, a framework of long-range order persists well into the transformation, despite extensive short-range disorder, and cooperative rearrangements involving distinct intermediate symmetries appear to be involved.

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AMORPHOUS TRANSITION METAL OXIDES

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The electronic properties of Transition Metal Oxides (T.M.O.) arise from the fact that Transition Metal Ions may exhibit several valence states. Electron transfer from low to high valence ions can take place and depending upon the competition between several parameters, electron localization or delocalization can be observed.

Delocalization occurs through electronic coupling between adjacent metal ions. This coupling can be described by a Transfer Integral "J". It depends on the overlapping between metal orbitals.

Two localization processes occur in amorphous TMO : The first one arises from the electron-phonon coupling "$\gamma$" and leads to the formation of small polarons. The second one arises from the structural disorder "$W_d$" and leads to the so called "Anderson localization".

In most amorphous TMO, J is rather small while $\gamma$ and $W_d$ are quite large so that localization prevails. The semiconducting properties of amorphous T.M.O. therefore arise from a thermally activated hopping process of small polarons in which the activation energy appears to be temperature dependent. Electron transfer can be also optically activated allowing the developpement of amorphous T.M.O. thin films in the field of display devices.

Discussion will take into account different kinds of amorphous T.M.O., i.e. glasses, thin films and gels.

# STRUCTURAL DIFFERENCES IN TWO GLASSY Ni-28 at-% P ALLOYS

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The density of metallic glasses is universally only a few percent less than the value for a crystalline material of similar composition. This is consistent with similar short range packing of the atoms in the glass and in the crystalline forms, and with similar near neighbor pair interactions. In the case of Ni-P glass, with approximately 28 at-% P, five stable or metastable structures are known to exist near this composition: $Ni_3P$, $Ni_5P_2$, $Ni_{12}P_5$, $Ni_7P_3$, and $Ni_2P$. It is not clear which form of short range order will be preferred in the glass, or indeed if the glass will be a mixture of two or more forms.

EXAFS spectra were obtained for d.c. and pulsed electrodeposited Ni-P samples of the same composition, and also for $Ni_3P$ and pure Ni. The Ni-P distances in the pulse plated samples were greater by approximately 0.1 A than those for the d.c. plated samples, while the Ni-Ni distances were about 0.1 A smaller. These results are in agreement with the conclusions from recent NMR measurements [1] suggesting that there are at least two forms of short range order in these glasses, and that the processing and thermal history of the samples determine the local configurations. The structural discontinuity between the two "glassy phases" indicate that mixing of structural states is unlikely.

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# THE ROLE OF NETWORK DIMENSIONALITY IN CHALCOGENIDE GLASSES

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In a solid containing covalent bonds, it is convenient to introduce the concept of covalent-network dimensionality. The network dimensionality may be defined as the number of dimensions in which the covalently-bonded (molecular) unit is macroscopically extended. Chalcogenide glasses come in all network dimensionalities, and can evidently even change network dimensionality during annealing processes.[1] Pressure-optical work in our lab on $GeS_2$ glass has indicated that this material is not a 3d-network (fused-silica-analog Zachariasen-type) glass, but instead an essentially-molecular glass with lower network dimensionality.[2] The optical and pressure-response consequences of network dimensionality in various amorphous chalcogenides will be discussed in this talk.

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PHOTOLUMINESCENCE AS A PROBE OF ELECTRONIC STATES IN NONCRYSTALLINE MATERIALS

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A variety of optical techniques have been used to probe electronic states in amorphous semiconductors. These include CW and transient absorption, scattering, luminescence, photoconductivity and double resonance measurements. Many of these experiments reveal strong similarities among amorphous materials, although not all are true glasses. For example, the luminescence properties of the amorphous alloy a-Si:H resemble those of the chalcogenide glasses $As_2Se_3$ and $As_2S_3$. At low temperatures, all have been found to have a high density of geminate recombination centers with strong lattice coupling, giving rise to a broad luminescence band deep in the gap. In addition there is a remarkable similarity in the spectral and intensity evolution following pulsed excitation, and in the thermal quenching behavior. In the chalcogenide glasses, specific charged defects intrinsic to the glass structure have been proposed as the radiative centers. In contrast, recombination in a-Si:H has been modelled as tunnelling between carriers localized in neutral band-tail states. I will discuss recent ns and ps time scale optical experiments that address these questions. For example, luminescence measurements using sub-band-gap excitation in a-Si:H have indicated the involvement of either a single charged site or exciton decay in sub-microsecond luminescence processes. Ongoing work on sub-nanosecond time scales in a-Si:H and chalcogenide glasses are examining the fastest radiative processes and providing more definitive information on the electronic states and the mechanisms involved in recombination in these materials.

# ISOMERIZATION MODEL FOR THE STAEBLER-WRONSKI EFFECT

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The Staebler-Wronski effects were examined by using the isomerization model in a Si-O-H--Si configuration (- is the covalent or ionic bond and -- is the hydrogen bond). When this configuration is exposed to light of a proper wave length, the Si-O-H bond will be isomerized to the metastable position because the bond angle between Si, O and H is estimated about 124° in free space. However, this bond angle will be changed due to the hydrogen bond, and they have metastable position. As the result, the hydrogen bond, H--Si is broken by exposing light. Then the remaining dangling bond on the Si atom creates a deep level and lowers the Fermi-level. This is the cause of photo induced dark conductivity change. On the other hand, since the hydrogen bond creation energy is estimated less than 0.43 eV, the broken bond easily recovers its original position by annealing at the below the deposition temperature

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# "LOW FREQUENCY RAMAN SCATTERING FROM VITREOUS AND MOLTEN $B_2O_3$"

by

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Integrated Raman intensities of bands between $\sim$0-900 $cm^{-1}$ have been obtained for molten $B_2O_3$ from 288-906°C. Emphasis was placed on the depolarized low-frequency contour (adjoining the exciting line) which is intense, broad, skewed to high frequencies, and displays a weak, broad shoulder centered between $\sim$ 100-150 $cm^{-1}$. The total intergrated contour intensity from 0-250 $cm^{-1}$ obeys the one-phonon Bose-Einstein (B.-E.) relation within 6%. The integrated intensity of the polarized 800 $cm^{-1}$ boroxol ring ($B_3O_6$) line, however, decreases with temperature rise yielding a $\Delta H^{\circ}$ value of 5.6±1.0 kcal/mole ring rupture, in satisfactory agreement with a previous valve of 6.4±0.4 kcal/mole, J. Chem. Phys, 72, 113 (1980). The low-frequency contour probably involves nonsymmetric collective modes of very large groups, rings, or cages, as well as librations of $BO_3$ and $B_3O_6$ groups, and the fact that it obeys the B.-E. distribution at temperatures for which $B_3O_6$ ring rupture is important indicates that aggregates which have $BO_3$ triangles and/or $B_3O_6$ rings as the basic units are involved. The peak frequency of the B.-E. corrected low-frequency contour was also observed to be constant $\sim$50 $cm^{-1}$, from -265°C to $\sim$200°C, but it falls rapidly near $T_g \approx$ 280°C, and then reaches a $\sim$27 $cm^{-1}$ limit above 400°C. This suggests that the force constants decrease upon melting because the anharmonicity increases due to the increased free volume of the melt.

# PROPERTIES OF AMORPHOUS HARD CARBON FILMS

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When carbon ions impinge on a substrate with kinetic energies in the range of 100 eV, films are deposited which can have high hardness and electrical resistivity, and are reasonably transparent.[1,2] Depending upon the conditions of deposition (not yet fully understood), the films may exhibit polycrystallinity, with regions having cubic structure and lattice constant suggesting "diamondlike" tetrahedral bonding. However, the films more often lack any crystalline structure, while still displaying the distinguishing features of hardness, resistivity, and transparency.

Production and characterization of amorphous hard carbon films at the Naval Research Laboratory will be described. Most of the experimental studies deal with partially hydrogenated films prepared by rf glow discharge decomposition of propane or acetylene. Deposition techniques using carbon ion beams and laser-produced plasmas are being investigated as well. The rf plasma deposited films are shown by STEM electron diffraction measurements to be amorphous. Typical Knoop hardnesses in the range of 800 and resistivities of order $10^8$ ohm-cm are obtained. The optical absorption coefficient rises gradually from low values in the infrared to about $10^5$ $cm^{-1}$ at 4 eV in the ultraviolet, giving the films a characteristic light brown color. Optical spectra and electronic properties will be discussed in relation to models of bonding structure and defect states.

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# AMORPHOUS-TO-CRYSTALLINE TRANSITION IN SILICON AND PARAMETERS CONTROLLING THE STRUCTURAL PROPERTIES OF PLASMA CVD FILMS

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## ABSTRACT

The paper will review some previous and most of the recent results on the transition between crystalline and amorphous phases in silicon. Quantitative experimental data show that below a crystallite size of $\sim 30$ Å, stress free microcrystalline silicon becomes thermodynamically unstable with respect to the amorphous phase. Theoretical considerations explain this behaviour in terms of reduction of the elastic lattice energy upon the crystalline-to-amorphous transition due to decrease of the stress associated with grain boundaries. Simple structural models illustrate this point.

During the film deposition in a glow discharge the formation of either amorphous or crystalline film (at the same deposition temperature) is controlled by the balance between silane decomposition versus its formation on the surface, and by the amount of non-thermal energy being dissipated into the surface of the growing films.

Last part of the talk will deal with the control of stress in the films during their deposition and with the influence of the stress on structural and related physical properties. Comparison of the results obtained for silicon with data which were found in other systems points towards a possible universality of some of the conclusions to be presented.

Detailed structural studies by means of high resolution electron microscopy will be included as well.

# THE FIRST SHARP DIFFRACTION PEAK, THE STRUCTURE AND THE LOCAL NATURE OF BONDING INTERACTIONS IN GLASSES

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A variety of glasses and disordered systems exhibit in their diffraction patterns a diffraction pre-peak (FSDP), usually centered around $S = 1.0\ \text{Å}^{-1}$. Most of existing interpretations of this feature correlate the FSDP with a particular real space lattice, intermolecular or cluster spacing.

An alternative explanation for the existence of FSDP will be suggested. It uses the concept of non-ergodicity and the phenomenon of localization in disordered systems. It will be proposed that due to the non-ergodic nature of the preparation process of disordered solids, the electronic interactions which eventually lead to the formation of bonds and to cohesion, extend over quite a small spatial volume around each atom. The local nature of these interactions will lead only to a finite range of real space correlations and it is this range that gives rise to FSDP. The existence of FSDP, when it is observed, might be therefore an important 'range' parameter of one-electron bonding interactions in glasses. Supporting evidence for the proposed model will be presented and discussed. It will include both the results of theoretical calculations of the electronic structure and the experimental observations.

# PROPERTIES AND STRUCTURE OF THE HYDROGENATED AMORPHOUS SILICON FILMS FORMED BY IONIZED-CLUSTER BEAM DEPOSITION

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Hydrogenated amorphous silicon films were formed by ionized-cluster beam deposition of silicon in relatively low gas pressure of hydrogen in a range of $10^{-5}$ - $10^{-4}$ Torr. Effective hydrogenation is due to the kinetic and the ionic charge effects of the cluster beams, which are characteristics of the ionized cluster beam deposition (1,2). For doped film formation, mixed hydrogen gas with phosphine or diborane of the order of 5000 vppm was used. P- or n-type films could be well reproducibly formed at practical deposition rate. The optical band gap of the films could be controlled in a range of 1.3 eV - 1.9 eV by changing hydrogen gas pressure. The films showed extended state conduction with well-defined activation energy. The photo conductivitiy increased with increasing the acceleration voltage during the deposition whereas the dark conductivity decreased with increasing the acceleration voltage. The films showed good adhesion, smooth surface thermally stable characteristics. Structual analysis showed that the film was mainly consisted of monohydrides. Number of this structure can be increased by the deposition at higher acceleration voltage. In contrast, $Si\text{-}H_2$ structure decreases at higher acceleration voltages.

In the paper we will discuss the dependences of the film properties and structures on the deposition conditions such as the acceleration voltage and the ionic charge of the ionized-cluster beams and hydrogen gas pressures. Emphasis will also be put on the difference in the deposition feature of amprphous silicon between ionized cluster beam deposition and other existence methods.

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# ON THE IMPORTANCE OF OXYGEN-OXYGEN INTERACTIONS IN SILICA STRUCTURES

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Oxygen-oxygen interactions are found to play an important role in determining the relative orientations of adjacent corner-sharing oxygen tetrahedra. Initial Monte Carlo studies showed that an exclusion principle based upon a minimum allowed O-O separation in adjacent tetrahedra drastically restricted the relative orientations such tetrahedra can assume. This ad-hoc criterion reproduced the experimentally observed Si-O-Si angle distribution determined from the structural data of a large number of silicas and silicates. Subsequent calculations using either (i) a Lennard-Jones 6-12 potential for O-O interactions, or (ii) Coulombic interactions between all atoms in adjacent tetrahedra, lead to quite similar results. Further studies suggest that, when extended structures are formed, this steric requirment alone causes additional and severe restrictions on the relative orientations of adjacent tetrahedra. In a first nearest neighbor cluster of five tetrahedra, we have four dimers and six trimers to consider and the O-O interactions at the trimer level leads to additional restrictions beyond those found for the dimers alone. Preliminary results on clusters including second nearest neighbors, confirm the trend towards enhanced restrictions on the orientations of adjacent tetrahedra. At this level, the size of the closed rings (e.g. with 4,5,6. etc. bridging oxygens) that would form is largely decided.

The relationships of the foregoing calculations to (i) the general requirement for extended silica structures in the amorphous-crystalline configurations and (2) the structure of vitreous silica immediately adjacent to thermally oxidizing Si and its transformation mechanism to bulk vitreous Si $O_2$ far from the interface are under consideration.